so, the formation of 2-methylcyclopentanone seems to be free from this effect. In solutions of cyclohexanone in cyclohexane, at 3130 Å., the quantum yields for both photoisomers decrease with decreasing concentration. The absolute value for 2-methylcyclopentanone from pure cyclohexanone is of the order of 0.03.

Two aspects of reaction 1 are of considerable interest. One is the mechanism by which the net transfer of a hydrogen atom from the 3 to 2 position or *vice versa* takes place. It seems likely that the process is intramolecular in nature and does not involve long-lived free-radical intermediates, as the addition of about 10% of cyclohexene to a 50% solution of cyclohexanone in cyclohexane caused no change in the rate of formation of 2-methylcyclopentanone. In order to determine whether it is the carbon atom that is α or β to the carbonyl group that appears in the methyl group in the product, the photolysis of cyclohexanone-2,2,6,6-d_4 is being investigated.

A second interesting point is the identity of the excited state which gives rise to reaction 1. Since the formation of 5-hexenal is capable of being quenched (by itself) while the formation of 2-methylcyclopentanone is not, it seems reasonable to suggest that these two reactions occur from two different electronic states of cyclohexanone. The failure to observe reaction 1 in the gas phase is not contrary to this suggestion as this reaction might easily have gone unobserved if its quantum yield in the vapor phase is as small as it is in the liquid. A more direct approach based on the emission of radiation to identify the excited states in the condensed phase is also under investigation.

Acknowledgment.—The authors are grateful to Drs. E. B. Whipple, R. L. Hinman, and D. Arnold of the Union Carbide Research Institute for the determination of the n.m.r. spectra.

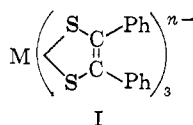IBM WATSON RESEARCH CENTER   S. CREMER
YORKTOWN HEIGHTS, NEW YORK   R. SRINIVASAN

Tris(*cis*-1,2-stilbenedithiolato)vanadium(VI) or Tris(dithiobenzil)vanadium(0). A Novel Vanadium Complex[1]

Sir:

We report here the characterization of a remarkable new vanadium complex, which is one member of a series of six-coordinate complexes with the general formula I with $n = 0$, 1, or 2, and $M = V$, Cr, Mo, or

$$M\left(\begin{array}{c} S \diagdown_C\diagup Ph \\ \| \\ S\diagup^C\diagdown Ph \end{array}\right)_3^{n-}$$

I

W.[2] Analytical and solution molecular weight data establish the correctness of I for the $n = 0$ complexes.[3]

Reduction of the $n = 0$ complexes ($M = $ Cr, Mo, or W) with $NaBH_4$ in diglyme gives the $n = 1$ complexes, which are reoxidized by air to the neutral materials. For $M = $ Mo, two reversible polarographic waves are observed in DMF.

The odd-electron (I) systems have $S = 1/2$ and show characteristic e.s.r. spectra. The $V(S_2C_2Ph_2)_3$ complex shows an eight-line e.s.r. spectrum in $CHCl_3$ solution, with $\langle g \rangle = 1.992$. The substantial isotropic hyperfine splitting of 61.6 ± 0.3 gauss due to ${}^{51}V$ ($I = 7/2$) strongly suggests that the unpaired electron is in a metal-based molecular orbital.[4] For comparison, the $M(S_2C_2Ph_2)_3{}^-$ complexes ($M = $ Cr, Mo, or W), in which the unpaired electron is in the next higher MO, show characteristic $\langle g \rangle$ values and electron-nucleus hyperfine splittings as follows: $M = $ Cr, $\langle g \rangle = 1.996$, $\langle a \rangle({}^{53}Cr) = 19.0 \pm 0.5$ gauss; $M = $ Mo, $\langle g \rangle = 2.011$, $\langle a \rangle({}^{95,97}Mo) = 11.2 \pm 0.4$ gauss; $M = $ W, $\langle g \rangle = 1.992$. The relative metal/ligand character of the two MO's in question is suggested by the normalized isotropic hyperfine splittings in the V ($n = 0$) and Cr ($n = 1$) complexes. The normalized splittings of 42 gauss/nm. for $V(S_2C_2Ph_2)_3$ and 60 gauss/nm. for $Cr(S_2C_2Ph_2)_3{}^-$ indicate that the higher MO has somewhat more metal character in the first-row complexes.[5]

The $V(S_2C_2Ph_2)_3$ complex has special significance in the problem of formulation of the ground states of bis and tris complexes containing bidentate, unsaturated sulfur-donor ligands.[6] The stability of $V(S_2C_2Ph_2)_3$ makes it clear that the oxidation-state formalism which requires $R_2C_2S_2{}^{2-}$ and high-oxidation-state metals cannot be applied consistently to these complexes, since the formalism in the V ($n = 0$) case would call for V(VI).[7] It would be unreasonable to suggest that the metal is effectively $3p^5$ in this complex. Further, $V(S_2C_2Ph_2)_3{}^{7a}$ cannot be the first example of a complex of this type in which the ligand is oxidized,

(1) Acknowledgment is made to the National Science Foundation for support of this research.

(2) R. B. King, *Inorg. Chem.*, **2**, 641 (1963), has reported the related complexes $Mo[S_2C_2(CF_3)_2]_3$ and $W[S_2C_2(CF_3)_2]_3$.

(3) The $n = 0$ complexes of V, Cr, Mo, and W were previously formulated as $M(S_2C_2Ph_2)_2$ on the basis of analytical results that were found to be in error [G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964)]. *Anal.* Calcd. (found): for $C_{42}H_{30}S_6V$: C, 64.82 (64.79); H, 3.89 (3.87); S, 24.73 (24.34). For $C_{42}H_{30}S_6Cr$: H, 3.89 (4.03); S, 24.69 (24.64). For $C_{42}H_{30}S_6Mo$: C, 61.28 (61.04); H, 3.68 (3.76); S, 23.38 (23.2); mol. wt., 823.1 (763). For $C_{42}H_{30}S_6W$: C, 55.36 (55.58); H, 3.33 (3.43). In addition, the complexes with M = Re, Ru, and Os appear to be tris and not bis as previously reported.

(4) The unpaired electron, although "metal-based," is almost certainly delocalized through the ligand system, since the ${}^{51}V$ splitting is considerably less than in $VO(H_2O)_5{}^{2+}$ [$\langle a \rangle({}^{51}V) = 118$ gauss: R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960)]. In fact, the ${}^{51}V$ splitting in $V(S_2C_2Ph_2)_3$ compares favorably with the splitting in $V(CN)_6{}^{4-}$ [$\langle a \rangle({}^{51}V) = 60$ gauss: J. M. Baker and B. Bleaney, *Proc. Phys. Soc.*, **A65**, 952 (1952)], where some delocalization through the CN^- system is expected.

(5) The ${}^{53}Cr$ splitting in $Cr(S_2C_2Ph_2)_3{}^-$ is larger than the splitting in $Cr(CN)_6{}^{3-}$ observed in $K_3[Co(CN)_6]$. For $Cr(CN)_6{}^{3-}$, $\langle a \rangle({}^{53}Cr) = 15.8$ gauss [K. D. Bowers, *ibid.*, **A65**, 860 (1952)].

(6) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, in press.

(7) The conventional oxidation-state formalism allows two limiting descriptions of complexes of such ligands. In the first, the metal is assigned a high oxidation state and is considered to be bonded to the ligand $R_2C_2S_2{}^{2-}$. In the second, the metal is assigned a low oxidation state, and the ligand is represented as $R_2C_2S_2$.

$$\begin{array}{c} R \diagdown \qquad S \\ \diagup^C \diagup \\ \mid \\ C \\ \diagup \qquad \diagdown\!\!\!\! \\ R \qquad S \end{array}$$
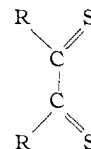
It is clear that for R = Ph (and presumably for other R's as well), neither limiting formulation satisfactorily describes the full range of bis and tris complexes of the ligand. The first formalism requires V(VI) in $V(S_2C_2Ph_2)_3$, while the second requires M(−1) and M(−2) in the anionic complexes, which is not appealing in any case and is certainly unreasonable in the bis complexes with M = Ni. It should also be noted that the $R_2C_2S_2$ formulation requires Ni(0) in $Ni(S_2C_2Ph_2)_2$, in which case we would expect a tetrahedral NiS_4 arrangement. However, there is evidence that the complex is planar [G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962)]. Structural work now in progress [M. R. Truter] should decide the issue.

(7a) NOTE ADDED IN PROOF.—The $V(S_2C_2Ph_2)_3$ complex has independently been characterized by A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki; private communication from Dr. R. H. Holm.

since the normalized hyperfine splitting due to the metal nucleus is among the largest observed to date in the bis and tris complexes containing bidentate, unsaturated sulfur-donor ligands.[6] As soon as definitive crystal structural work now in progress[8] is completed, we shall attempt to derive a molecular orbital scheme which will be able to formulate consistently these interesting new complexes.

(8) R. Eisenberg and J. A. Ibers, private communication.

(9) National Science Foundation Predoctoral Fellow, 1963–1964.

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A Quantitative Scale of Acceptor Strengths from Fluorine Nuclear Magnetic Resonance Shielding[1]

Sir:

The shielding of the fluorine atom in a *p*-fluorophenyl derivative, p-FC_6H_4X, has been shown to be a highly sensitive measure of the power of the group X to contribute or withdraw electronic charge from the benzene ring in its ground electronic state.[2] If the group X is formed by interaction between a common donor function and a series of Lewis acids, the relative polarizing power of the X group, as measured by the shielding, should reflect the strength of this interaction. With a donor function of minimum steric requirements, this physical measurement can potentially provide an "intrinsic" scale of acceptor strengths with useful chemical applications.

We report here the result of preliminary studies which appear to establish definitely the potential of this method. The donor molecule used is *p*-fluorobenzonitrile (FBN). Brown[3] has demonstrated previously the minimal steric requirements of the spike-shaped nitrile function.

Figure 1 records the results of a series of experiments carried out with an approximately constant concentration (~ 0.4 M) of FBN and varying concentrations of *p*-fluorophenylboron dichloride. These experiments constitute a "double-label" investigation of the complexing. The shielding parameters for the single observed fluorine signal (obtained at 40 Mc.) from both acid and base are plotted in Fig. 1 *vs.* the stoichiometric acid–base ratio (a/b). For a rapid reversible equilibrium, the fluorine signal is the weighted average of the shielding parameters for complexed and uncomplexed acid or base.[4] On complexing, the FBN signal appears at decreased field strength, and the acid fluorine signal at increased field, as anticipated for the flow of charge from base to acid.[5] The concentration dependence of

(1) This work was supported in part by the Office of Naval Research.

(2) *Cf.* R. W. Taft, *et al., J. Am. Chem. Soc.*, **85**, 709, 3146 (1963), and references cited therein.

(3) H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 2934 (1950); note Fig. 3 and 4 given therein.

(4) J. S. Pople, W. A. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 218.

(5) In the valence bond description of the donor–acceptor complex (*cf.* R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962)).
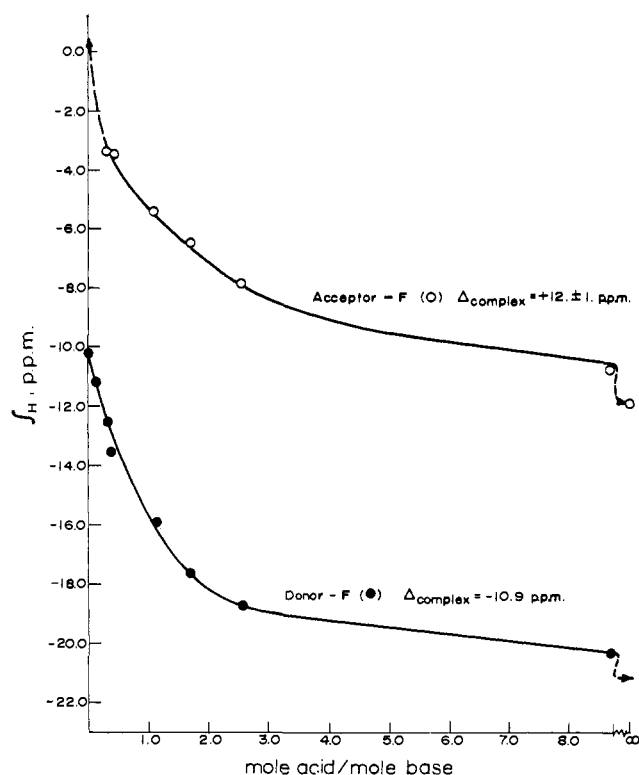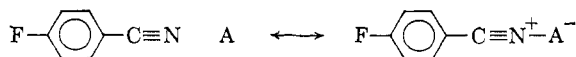
F—⟨○⟩—C≡N   A   ⟷   F—⟨○⟩—C≡N⁺—A⁻

Fig. 1.—Double-label investigation of donor–acceptor complexing between *p*-fluorophenylboron dichloride and FBN in methylene chloride at 25°; theoretical curves based on $K_{form} = 6.0 \pm 0.6$ M^{-1} and indicated limiting shifts.

both signals is satisfactorily described by assuming the formation of a 1–1 complex having a formation constant of 6.0 ± 0.6 M^{-1}, as illustrated in Fig. 1 by the agreement between experimental points and the theoretical curves.[6] The change in shielding parameters $\Delta_{complex}$ between completely complexed and uncomplexed FBN is given in Table I. The corresponding (estimated[6]) value for the *p*-fluorophenylboron dichloride is $\Delta_{complex} = +12 \pm 1$ p.p.m.
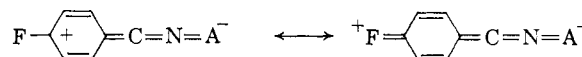
TABLE I

F N.M.R. SHIELDING PARAMETERS OF *p*-FLUOROBENZONITRILE DONOR–ACCEPTOR COMPLEXES. A QUANTITATIVE MEASURE OF ACCEPTOR STRENGTHS

Acceptor	$\Delta_{complex}$,[a] p.p.m.	ΔH_d,[b] kcal./mole	K_f, M^{-1}
None	0.00^c	0.0	...
$B(CH_3)_3$	...	15.3 ± 0.2	Very small
BF_3	-9.25^d	25.0 ± 1.0	76 ± 20
p-$FC_6H_4BCl_2$	-10.90^d	...	6 ± 0.6
B_2Cl_4	-11.50^e	...	$\geqslant 5000$
BCl_3	-12.30^e	30.8 ± 0.2	$\geqslant 5000$
BBr_3	-13.10^e	32.0 ± 0.2	$\geqslant 5000$

[a] Experimental error ± 0.10 p.p.m.   [b] Reference 10. $\int^{p\text{-}CN}_{H}$ $= -10.30$; *cf.* ref. 2 for symbolism.   [d] Computed value, *cf.* ref. 6.   [e] Observed value.

the following additional (F n.m.r. shielding sensitive; *cf.* ref. 2) forms are expected to contribute to the ground electronic state.

F—⟨+ ○⟩=C=N=A⁻   ⟷   ⁺F=⟨○⟩=C=N=A⁻

(6) The theoretical curve is based upon calculations of best fit of the data by the Penn State IBM 7074 computer using the 1–1 formation constant and the limiting F n.m.r. shift as adjustable (but concentration-independent) parameters. We are indebted to Dr. Stanton Ehrenson, Brookhaven National Laboratory, for this program. Any small medium effects are unimportant for present purposes.